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# PATENT SPECIFICATION

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## (54) POLYURETHANE FOAMS

- 5 (71) We, W.R. GRACE & CO., a Corporation organized and existing under the laws  
of the State of Connecticut, United States of America, of Grace Plaza, 1114 Avenue of the  
Americas, New York, New York 10036, United States of America, do hereby declare the  
invention for which we pray that a patent may be granted to us, and the method by which it  
is to be performed, to be particularly described in and by the following statement:
- 10 This invention relates to polyurethane foam production.
- 15 Polyurethane foams are now quite commonly employed for use in surgery and other  
applications involving contact with the body. Generally such foams have some hydrophilic  
character by the inclusion of a separate hydrophilic additive into a hydrophobic  
reacting polyoxyethylene polyols with a polyisocyanate and low, i.e., near stoichiometric  
amounts of water. A catalyst is generally employed in such reactions. Foams based on  
non-catalytic reactions have also been prepared using linear polyoxyethylene diols,  
diisocyanate and varying amounts of water. Hydrophilic cross-linked polyurethane foams  
20 may be prepared simply by reacting an isocyanate capped polyoxyethylene polyol with large  
amounts of water greatly in excess of the stoichiometric amounts needed for curing. These  
foams generally contain residual by-products which are loosely bound into the foam and  
which easily extract during use.
- 25 It has been discovered that polyurethane foams contain residual aromatic amines which  
are believed to result from hydrolysis of isocyanates during and subsequent to the foaming  
process, and possibly due to hydrolysis of the foam during storage. For example, both  
one-shot and prepolymer foams employing toluene diisocyanate have been found to contain  
the corresponding amine, namely toluene diamine (TDA). It is believed that foams  
employing other aromatic polyisocyanates contain the corresponding polyamine. The term  
"aromatic amine" as used herein is intended to refer primarily to TDA but it also includes  
30 other aromatic amines formed from the corresponding polyisocyanates. According to the  
present invention the amount of aromatic amine is reduced by introducing a "scavenger",  
generally prior to foaming, said scavenger being a material which can survive the foaming  
reaction to react with aromatic amines as they are generated. Accordingly the present  
invention provides a process for preparing a fluid-permeable (as hereinafter defined)  
35 polyurethane foam derived from an aromatic poly-isocyanate which comprises incorporat-  
ing a scavenger for aromatic amine either in:
- (a) a mixture of an aromatic poly-isocyanate, a polyether or polyester polyol and water  
in which case the index of said scavenger in the mixture is from 0.01 to 4, generally from 0.2  
to 4, and the index of said aromatic poly-isocyanate in the mixture is from 110 to 96, or  
40 (b) a mixture of a prepolymer comprising polyether or polyester units capped by an

aromatic poly-isocyanate, and water, in which case the scavenger is present in an amount not more than 8 parts by weight based on the weight of the functional groups of the scavenger, per 100 parts by weight of said prepolymer, and causing the resulting mixture to react, or in (c) the foam obtained by reacting a mixture as defined in (a) or (b), which mixture did not contain scavenger.

It has been discovered that the most effective scavengers are aliphatic (including cycloaliphatic and aryl aliphatic) mono- or poly-isocyanates, especially diisocyanates, such as bis(cyclohexylisocyanato)methane (4,4'-methylenebiscyclohexyl diisocyanate), isophorone diisocyanate and bis (3-methyl-4-isocyanatocyclohexyl)methane, as well as tris (6-isocyanatohexamethylene)-biuret and isocyanate derivatives of condensed fatty acids but other aliphatic isocyanates as well as other materials which are capable of reacting with an aromatic amine and which react more slowly with water (or not at all) than the aromatic polyisocyanate employed, can be used. For example, organic oxirane compounds such as epoxidised soya bean oil and epichlorohydrin epoxy resins derived from bisphenol A such as EPON 828 from Shell Oil Co.; organic anhydrides, in particular a carboxylic acid anhydride such as phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, alpha-olefin/maleic anhydride copolymers, poly(maleic anhydride) and oligomers thereof, styrene/maleic anhydride copolymers and alkyl vinyl ether/maleic anhydride copolymers; acyl halides such as benzoyl chloride, octanoyl chloride and sebacoyl chloride; organic sulphonyl halides such as benzene sulphonyl chloride; and carbodiimides such as "Isonate" (Registered Trade Mark) 143 L (by Upjohn) and "Staboxo" (Registered Trade Mark) I (bis)2,6-diisopropylphenylcarbodiimide by Naftone, Inc. The scavengers can, of course, be used in mixtures or blends with one another if so desired. The preferred scavenger reacts only slowly with water, polyols or isocyanate groups so as to survive the initial polymerisation reaction, but is capable of reacting rather rapidly with by-product aromatic amine moieties during the drying and/or storing of the polyurethane product.

Although the theory of the formation of the aromatic amines as well as the activity of the scavenger are not clearly understood, it appears that aromatic polyisocyanates and possibly their reaction products containing urea and urethane linkages are hydrolysed to produce free aromatic amines which can be leached from the polyurethane foam. The aliphatic diisocyanate or other scavenger is believed not to complete successfully with the aromatic polyisocyanate for functional groups during the polymerisation reaction. Therefore the aliphatic isocyanate survives polymerisation and is believed to form urea addition products with aromatic amines as these are produced. These products appear to be more difficult to leach from the polyurethane foam and are also not believed to present a potential health hazard. It has also been found that the resulting foams contain minor amounts of aliphatic amines which are hydrolysis products of the aliphatic isocyanates. However, the aliphatic amines are not believed to present the potential health problems raised by the aromatic amines.

A number of factors are important in reducing levels of TDA and optimising the effect of the scavenger. In general the residual aromatic amine content should be reduced to below 500 ppm. For example, foams which are stored while still wet tend to exhibit a higher level of TDA than the corresponding foams stored following drying. Up to 8% by weight of scavenger based on the weight of the prepolymer is used; amounts of 4% by weight or less are frequently satisfactory. Generally amounts range from 0.01 to 8% by weight and preferably 0.1 to 4% by weight. It should be understood that the weight percentage is based on the weight of the NCO groups, in the case of an aliphatic isocyanate, and does not include the residual portions of the isocyanate molecule such as the aliphatic hydrocarbon residue in the case of isophorone diisocyanate. The above percentages also apply to the other organic amine binding agents employed. Where an acyl chloride is employed, the percentage is based on the functional groups (-GCl). Also, the use of certain catalysts has been found to be detrimental; accordingly it is preferred that any catalyst employed be a "mild" catalyst which promotes reaction between the aromatic polyisocyanate and hydroxyl groups of the polyol and permits the foaming reaction to proceed at a reasonable rate but does not cause undesirable side reactions involving either the aromatic or aliphatic isocyanate such as biuret formation or trimerisation, or cause the aliphatic isocyanate to be incorporated into the polymer. If conventional strong catalysts such as tin salts are employed, less than the usual amount should be used.

The optimum scavenger to be employed with a particular aromatic polyisocyanate can be determined by dissolving the corresponding amine and the scavenger at equivalent (or greater) stoichiometric levels, i.e. enough of the scavenger is employed to react with one hydrogen atom in each  $\text{NH}_2$  group, in a common inert solvent. Within 16 hours at ambient temperatures the scavenger and amine should undergo a reaction which is essentially irreversible and complete. Additionally, when dispersed in water, the scavenger should generally exhibit a reaction rate with the water (at  $25^\circ\text{C}$ ) which is less than about  $10^{-2}$  times

the reaction rate of the aromatic polyisocyanate with the water and preferably  $10^{-3}$  –  $10^{-5}$  times. In carrying out the test, separate aqueous solutions or dispersions of the aromatic polyisocyanate and scavenger can be prepared at a concentration of, say,  $10^{-2}$  moles/litre. The rate of reaction can be measured at, say, 25°C. In the event either the scavenger or aromatic isocyanate is insoluble in water; the test can be carried out using constant agitation and suitable surfactants, or a suitable water-miscible cosolvent can be employed. It is believed that the above test procedure will furnish a useful guide, i.e. a "rough screen" in selecting useful scavengers. However, due to the complexity of the foaming process, the determination of utility of any particular scavenger should be based on actual runs.

The foams produced according to the present invention can be rigid, semi-rigid or flexible. Generally, the foams possess a fluid-permeable skin. By "fluid-permeable", as used herein, is meant that a section of foam (1 inch thick) sliced parallel to the surface and embodying said surface will exhibit a permeability to air of at least 0.25 ft.<sup>3</sup>/minute/ft.<sup>2</sup> of foam using a pressure differential of 0.002 atmosphere. Similar test conditions are described in ASTM D-737 for measuring the permeability of fabrics. By contrast, foams having a fairly dense skin will measure less than about  $10^{-3}$  ft.<sup>3</sup>/minute/ft.<sup>2</sup> of foam using the above test.

In a preferred embodiment of the invention the process comprises foaming (under conventional conditions) a mixture comprising: a) an aliphatic isocyanate and b) a urethane prepolymer having polyether or polyester backbone segments capped with an aromatic polyisocyanate, the aliphatic isocyanate being present in an amount not exceeding about 8 parts, preferably not exceeding about 4 parts by weight based on the weight of the functional groups of the aliphatic isocyanate per 100 parts by weight of said prepolymer, and water. The lower limit is not critical; it is determined by the degree of scavenging activity desired and also by the nature of the aliphatic isocyanate. Generally, a level of not less than 0.01 parts by weight should be employed.

Suitable aliphatic isocyanates include cycloaliphatic isocyanates or aralkyl polyisocyanates as well as straight or branched aliphatic isocyanates, e.g. xylene- $\alpha$ '-diisocyanate, n-dodecyl isocyanate, ethylene diisocyanate, n-butyl isocyanate, cyclohexyl isocyanate, trimethylene-diisocyanate, dicyclohexyl methane-4,4'-diisocyanate, isophorone diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexane diisocyanate and bis(3-methyl-4-isocyanatocyclohexyl)methane and mixtures thereof.

In preparing foams by the prepolymer technique, the prepolymer is generally admixed with a suitable blowing agent (e.g. water) and optionally a catalyst and other additives (e.g. fire retardants) depending on the ultimate properties desired in the foam. The amount of water employed as a blowing agent is generally from about 0.4 moles of H<sub>2</sub>O/mole of NCO groups to about 1,000 moles of H<sub>2</sub>O/mole of NCO groups, for example 6.5 moles to 390 moles. In determining the amount of water or aqueous reactant such as an aqueous slurry, suspension, or emulsion or an aqueous solution containing water-soluble material, the "mole of NCO groups" refers to the aliphatic NCO groups of the scavenger as well as the NCO groups contributed by the prepolymer or by the aromatic polyisocyanate in a one-shot reaction mixture, but does not include the NCO groups theoretically required to react with all the hydroxyl groups of the polyol employed in the one-shot process. For one-shot foams, the amount of water employed is preferably from about 0.40 to about 0.55 moles of H<sub>2</sub>O/mole of NCO groups (exclusive of NCO groups required for reaction with the polyol). In preparing foams by the prepolymer process the amount of water employed is preferably from about 0.40 to about 1.0 moles H<sub>2</sub>O/mole of NCO groups.

The urethane prepolymer employed comprises polyether or polyester backbone segments capped with an aromatic polyisocyanate (e.g. toluene diisocyanate; TDI). Suitable polyether prepolymers include the polyalkylene oxide ethers, such as the reaction products of ethylene oxide, propylene oxide, butylene oxide, styrene oxide, picoline oxide or methyl glycoside, with a compound containing two or more reactive hydrogens, such as water, resorcinol, glycerol, trimethylol propane, 1, 2,6-hexanetriol, pentaerythritol, sorbitol, ethylene glycol, diethylene glycol and triethylene glycol; typically the prepolymer is the reaction product of a polyoxyethylene polyol, especially a glycol, and a monomeric alcohol having at least 3 hydroxyl groups per molecule, especially an aliphatic alcohol having 3 hydroxyl groups per molecule, said reaction product being capped with an aromatic polyisocyanate. Other polyethers include polyoxypropylene glycol, polyoxyethylene glycol, polyoxybutylene glycol, polyoxyethyleneoxypropylene glycol, polyoxyethyleneoxybutylene glycol and polyoxypropyleneoxybutylene glycol. Hydrophilic polyethers are prepared.

Preferably, the polyether urethane prepolymers employed are hydrophilic in that at least 40 mole % of the oxyalkylene units in the prepolymer backbone are oxyethylene units with the balance being oxypropylene, oxybutylene or other oxyalkylene units. In the resulting polyurethane foams, the branch-points of the polymer chains are connected by essentially

linear polyoxyalkylene chains containing at least 40 mole % of oxyethylene units (excluding initiators at branch-points). Preferably, the oxyethylene content is from about 55 or 60 to 75 mole %. At oxyethylene levels of 40-60 mole %, it may be desirable to use a surfactant to promote dispersion of the prepolymer in water prior to foaming. Conventional surfactants for this purpose can be used, for example non-ionic surfactants, in particular polyether based surfactants such as those known under the Registered Trade Mark Pluronic derived from polyether alcohols as well as those derived from a higher aliphatic alcohol such as stearyl alcohol, and a polyether alcohol and silicone surfactants, for example derived from a silicone ester and a polyether alcohol.

Suitable prepolymers can be prepared by capping a polyoxyalkylene polyol with an excess (generally between about 1 to about 4, preferably about 2 to about 3, isocyanate groups to hydroxyl group) of aromatic polyisocyanate in a conventional manner, typically in an inert moisture-free atmosphere at 0° to 120°C for, say, 20 hours. Prior to capping, the polyol suitably has a molecular weight of from 200 to 20,000, preferably from 300 or 600 to 6,000. The hydroxy functionality of the polyol and the corresponding isocyanate functionality following capping is generally from 2 or 3 to, say, 8. If foams are formed from prepolymers with an isocyanate functionality of about 2, the resulting foam is essentially linear and does not have as much tensile strength as crosslinked foams. Accordingly, if the isocyanate functionality is about 2, a crosslinker can be employed, for example by addition to the water in which the prepolymer is dispersed, although the linear non-crosslinked foams can be prepared, to minimise adverse reactions involving the aliphatic isocyanate, any crosslinkers employed should desirably be aliphatic polyols (e.g. TMOP (trimethylol propane), glycerol or pentaerythritol) rather than amines.

Examples of suitable polyols (to be capped with polyisocyanates) include: (A) essentially linear polyols formed, for example, by reaction of ethylene oxide with water, using ethylene glycol or higher molecular weight glycols as an initiator. Where the linear polyethers are derived from mixtures of ethylene oxide with, e.g., propylene oxide, the polymer can be either a random or a block copolymer and the terminal units can be either oxyethylene or oxypropylene.

(B) those with a hydroxy functionality of 3 or more. Such polyols are commonly formed by reacting alkylene oxides or mixtures, as described above, with a polyfunctional initiator such as trimethylolpropane or pentaerythritol.

(C) linear or branched polyfunctional polyols as exemplified in A and B above prepared together with an initiator or crosslinker, for example a mixture of polyethylene glycol (m. w. say 1,000) with trimethylolpropane, trimethylolethane or glycerine. This mixture can be reacted subsequently with excess polyisocyanate. Alternatively, the linear or branched polyols (e.g. polyethylene glycol) can be reacted separately with excess polyisocyanate. The initiator, e.g. trimethylolpropane, can also be reacted separately with polyisocyanate. Subsequently, the two capped materials can be combined to form the prepolymer.

Suitable polyisocyanates useful in preparing prepolymers include polyarylisocyanates such as "PAPI" (Registered Trade Mark) triphenylmethane-4, 4', 4'-triisocyanate, benzene-1,3,5-triisocyanate, toluene-2,4,6-triisocyanate, diphenyl-2,4,4'-triisocyanate, xylene diisocyanate, chlorophenylene diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethoxy-4, 4'-biphenylene diisocyanate, 2,2',5,5'-tetramethyl-4,4'-biphenylene diisocyanate, 4,4'-methylenebis(phenylisocyanate), 4,4'-sulphonylbis(phenylisocyanate), 4,4'-methylene di-ortho-tolylisocyanate, toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, commercial mixtures of toluene-2,4- and 2,6-diisocyanates, m-phenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,5-naphthalenediisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-phenylenediisocyanate, 4-chloro-1,3-phenylene-diisocyanate, 4-bromo-1,3-phenylenediisocyanate, 4-ethoxy-1,3-phenylenediisocyanate, 2,4'-diisocyanatodiphenylether, 4,4'-diisocyanatodiphenylether, and 4,6-dimethyl-1,3-phenylenediisocyanate.

Useful polyester polyols include the reaction product of polyfunctional organic carboxylic acids, for example dicarboxylic aliphatic acids such as succinic, adipic, sebacic, azelaic, glutaric, pimelic acids and dicarboxylic aromatic acids such as phthalic acid, terephthalic acid and isophthalic acid as well as "dimer acids" such as the dimer of linoleic acid and hydroxyl-containing monocarboxylic acids such as ricinoleic acid or anhydrides thereof and polyhydric alcohols for example monomeric polyhydric alcohols such as glycerol, 1,2,6-hexane triol, ethylene glycol, trimethylol propane, trimethylol ethane, pentaerythritol, propylene glycol, 1,3-butylene glycol, and 1,4-butylene glycol. Generally these polymers have a molecular weight of 300-6000; polyols such as glycerol, TMP, and pentaerythritol can be employed to provide crosslinking. Typically the hydroxyl number will be 50-100 although values as high as 450 can be used in preparing rigid foams.

- Alternatively a one-shot process is used by foaming (using conventional techniques) a mixture typically comprising: a) aliphatic isocyanate, as scavenger for aromatic amine, b) aromatic isocyanate, c) a polyether or polyester polyol, and d) a catalyst system for promoting reaction between the aromatic polyisocyanate and the hydroxyl groups of the polyol, as well as water. In the mixture the aliphatic isocyanate index is from 0.01 to 4, generally 0.2 to 4, and the aromatic isocyanate index is from about 110 to about 96 especially about 99.8 to about 96.
- The expression "index" is used conventionally to indicate the ratio of the actual amount of aromatic or aliphatic isocyanate in the reaction mixture to the theoretical amount of isocyanate needed for reaction with all active hydrogen compounds present in the reaction mixture, multiplied by 100. Of course, for scavengers other than the isocyanates the index indicates the ratio of equivalents of the scavenger group to the equivalents of all active hydrogen compounds initially present in the reaction mixture, multiplied by 100.
- Conventional catalyst systems can be employed in conventional manner in preparing the one-shot foams of the invention. However, it has been found that many catalysts increase the amount of aromatic amines in the foams and accordingly the amount of catalyst employed should be held to a minimum consistent with obtaining a desirable rate in the foaming reaction as well as desirable properties in the finished foam. As discussed above, suitable catalysts should promote reaction between the polyol and the NCO groups of the aromatic polyisocyanate and should be employed under conditions where detrimental side reactions (e.g. trimerisation, dimerisation and biuret formation) are minimised. Conventional catalysts for promoting the NCO/alcohol reaction are set forth at Table LXX (page 212) of Saunders and Frisch, *Polyurethanes: Chemistry and Technology* (Part I), 1962, John Wiley & Sons; the Table below illustrates some suitable amounts thereof (in parts of catalyst/100 parts by weight of the polyol) is set forth below. According to conventional practice, catalysts are frequently used as mixtures and thus the actual amounts employed may vary considerably; the total amount should be kept to a minimum.

<i>Tertiary Amines</i>	<i>Catalysis</i>		<i>Miscellaneous Catalysts</i>
	<i>Tin Salts</i>	<i>Fe Salts</i>	
N-ethylmorpholine (0.2-1.0)	Stannous octoate (0.01-0.5) Dibutyltindiacetate (0.01-0.5)	Ferric 2-ethylhexanoate (0.05-1.0) Ferric chloride (0.03-1.0) Ferric acetylacetonate (0.03-1.5)	Cobaltnaphthenate (0.01-1.0) Tetrabutyl Titanate (0.01-1.2) Lead oleate (0.01-1.0) Diethylenetriamine (0.2-1.5)
Triethylenediamine (0.05-1.5)	Dibutyltindilaurate (0.01-0.5) Dibutyltindioctoate (0.01-0.5)		
Triethylamine (0.3-1.5)			
N,N-dimethyl-N',N'-dimethyl-1,3-diaminobutane (0.2-1.0)			

In the one-shot process all of the ingredients, e.g. the polyether or polyester polyol, the aromatic polyisocyanate, the aliphatic isocyanate, the blowing agent, catalyst, and any additional components such as UV absorber, surfactant, fire retardant additive and fillers, are mixed together and poured onto a surface or into a mould where foaming takes place according to conventional procedures (see, for example, United States Patent No. 3,790,508 and British Patent Specification No. 1,368,625). Suitable aromatic and aliphatic isocyanates, and polyols are as described above for the prepolymer process.

After the foam has been prepared it is desirably dried. It is also possible to treat the foamed polyurethane with a scavenger. This can be done by imbibing the scavenger into the product using a liquid vehicle such as water or an organic solvent or by exposing the product to the scavenger in the form of a gas, vapour or aerolised spray medium.

The foams of this invention are useful for, *inter alia*, decorative, cushioning, insulative, sound deadening, protective and fire retardant surfaces. Accordingly, these foams may form strippable coatings for protecting articles during handling and shipment. Also, because the foams are easily sterilised and are low in undesirable residuals, they find great utility as household, industrial and/or health care, cosmetic, dental or biomedical/surgical products. The feature of fluid permeability of these materials renders them attractive for apparel.

Catalysts, antioxidants and other chemical reactants may be supported on the foams for use in, for example, enzymatic reactions, fuel cells, filters, water or blood purification, extraction applications and in separation systems.

#### Examples 1-8

##### *Use of various aliphatic diisocyanates to reduce toluene diamine (TDA) levels in polyurethane foams*

Polyurethane foams were prepared using the prepolymer technique by reacting 200 g of Prepolymer A, B, or C (described below) with 200 g of water containing 4 g of surfactant in the presence of the aliphatic isocyanate specified in Table I. With the exception of Examples 6-8, the surfactant employed was Pluronic L-62 (BASF-Wyandotte), a nonionic polyether-based surfactant. In Examples 6-8 the surfactant was "Brij" (Registered Trade Mark) 72 (Atlas Chemicals Division of ICI, America, Inc.), a stearate surfactant. In the control foam using Prepolymers B and C, the Brij stearate surfactant was also employed. In the control foam using Prepolymer C as well as in Example 8, the amount of Brij surfactant employed was about 0.5 weight percent based on the weight of the prepolymer.

Prepolymer A was prepared by capping a mixture of trimethylolpropane (TMOP) and "Carbowax" (Registered Trade Mark) 1,000 (a polyoxyethylene glycol, Union Carbide and Chemicals Corp.) with toluene diisocyanate (TDI). Sufficient amounts of the mixtures were employed so that on the basis of molar equivalence the ratio of TDI/TMOP/glycol was 7.1/1/2. Analysis of the prepolymer for free TDI showed it to contain 3% by weight. The TDI was added in two stages. First, sufficient TDI was added to react with 95% of the hydroxyl groups followed by addition of the remaining portion of the TDI. Several hours was allowed between additions to promote chain extension in the prepolymer.

Prepolymer B was prepared using the same reactants as Prepolymer A except that the TDI/TMOP/glycol ratio was 6.7/1/2. The prepolymer contained 1% by weight of free TDI.

Prepolymer C was prepared according to the method used to prepare Prepolymer A except that ethylene glycol was used as an additional reactant. The ratio of reactants used was TDI/TMOP/polymeric glycol/ethylene glycol of 8.6/1/2/1.

The foams prepared as described above were analyzed for TDA by extracting 20 g of each foam 7 times with hot water followed by evaporation of the water. The extraction technique consisted of immersing 20 g of foam in 150 ml of deionized water at 38°C in a beaker for 5 minutes while compressing the foam several times with a spatula. This procedure was repeated 7 times with fresh water, ringing the foam as dry as possible between extractions. The combined extracts were filtered to remove any solid particles of foam and concentrated to approximately 50 ml in a rotary evaporator. The concentrate was evaporated to dryness in a beaker on a hot plate to obtain from about 0.134 g to about 0.330 g of dry extract. At no time was the temperature allowed to exceed 60°C. The TDA content of the extracts was determined and the results are set forth in Table I.



TABLE I

Example	Prepolymer	Aliphatic Isocyanate (%)	Extract (Weight %)In Extract (PPM)	Aromatic Amine (tolylene diamine)	Calculated Amount (PPM) of tolylene diamine in original form
Control	A	none	1.40	2590	36
1	A	*IPDI (0.5%)	1.38	1980	27
2	A	IPDI (4%)	1.08	1330	14
3	A	**MBDI (1%)	1.65	1180	20
4	A	MBDI (8%)	0.97	none detectable	none detectable
5 (Control)	A	none	0.77	1300	10
6	A	IPDI (5%)	0.67	none detectable	none detectable
Control	B	none	1.26	2270	18
7	B	IPDI (5%)	0.84	none detectable	none detectable
Control	C	none	1.20	1000	12
8	C	IPDI (5%)	0.76	none detectable	none detectable

\*IPDI = isophorone diisocyanate

\*\*MBDI = 4,4'-methylenebis (cyclohexyl isocyanate)

From the above Table it can be seen that for the isocyanate foam of Example 1, the initial diamine level, calculated at 36 ppm, decreased significantly as the amount of aliphatic isocyanate employed was increased. Comparison of Examples 1, 2 and 6 shows a steady reduction of 27 to 14 to the point where none was detectable. Similarly for methylenebis (cyclohexyl isocyanate) comparison of Examples 3 and 4 shows a similar decline. This decline is unexpected because each of the aliphatic diisocyanates was difunctional and some participation in the polymerisation reaction would seem probable. However, despite the presence of the exothermic polymerisation conditions, the presence of the aliphatic isocyanate still exhibited a significant influence on the amount of residual total extract and free tolylene diamine in the foam.

#### Examples 9-18

#### Preparation and Analysis of One-Shot Polyurethane Foams

15	Trade name designations in Examples 9-18 are as follows:		15
	"NIAx" (Registered Trade Mark) Polyol 1646- (Union Carbide)	ethylene oxide/propylene oxide copolymer	
20	NIAx Polyol 60-58 (Union Carbide)	- ethylene oxide/propylene oxide copolymer	20
25	NIAx LG-56 (Union Carbide)	- propylene oxide polyol (m. w. $\approx$ 3,000)	25
30	Formrez 50 (Witco Chemical Co.)	- polyester (adipic acid/diethylene glycol) glycol. m. w. $\approx$ 2,000, hydroxyl number m.w. = 2,000, hydroxyl number = 50	30
	"Freon" (Registered Trade Mark) (DuPont)	- trichlorofluoromethane	
35	Silicone L-520 (Union Carbide)	- hydrolyzable silicone surfactant (silicone ester/polyether alcohol reaction product)	35
40	Silicone L-5320 (Union Carbide)	- silicone surfactant	40
45	NIAx Catalyst A-1 (Union Carbide)	- tertiary amine/glycol admixture	45
	"DABCO" (Registered Trade Mark) (Air Products)	- triethylenediamine	
50	XDI-1421 (The Dow Chemical Co.)	- polyoxyethylene triol (> 50% end-capped with secondary hydroxyl groups)	50
55	"Hylene" (Registered Trade Mark) (DuPont)	- 1,1'-methylenebis(4-isocyanatocyclohexane)	55
	DDI-1410 (General Mills)	- stearic acid dimer diisocyanate	
60	Fryol FR-2 (Stauffer)	- tris-2,3-dichloropropyl phosphate	60
65	"Armeen" (Registered Trade Mark) (Armak Co.)	- D-16-D- dimethylhexadecylamine	65

5 Foams (designated A-E) were prepared using the one-shot technique and formulations as described below. Five sample foams were prepared from each formulation and the residual aromatic amine content from the five samples was averaged to give the values shown in Table II (below). Also, five control foams (no additive) were prepared from each formulation with the aromatic amine values shown in Table II being the average of the five. 5 In Table II the aliphatic isocyanate employed in the odd-numbered examples was Hylene W. The aliphatic isocyanate employed in the even-numbered examples was DDI-1410. The foam formulations employed in the examples are as follows: Formulation A (Examples 9, 10); Formulation B (Examples 11, 12); Formulation C (Examples 13, 14); Formulation D 10 (Examples 15, 16); and Formulation E (Examples 17, 18). 10

TABLE II

15	Example	Residual Aromatic Amine (ppn)	Residual Aromatic Amine in Control Foams (No Additive) (ppn)	15
	9			
20	2,4	26.3	44.3	20
	2,6	54.4	54.9	
	10			
25	2,4	22.3	44.3	25
	2,6	47.6	54.9	
	11			
30	2,4	11.6	53.6	30
	2,6	43.1	96.1	
	12			
	2,4	46.0	53.6	
	2,6	101.7	96.1	
35	13			35
	2,4	44.1	55.3	
	2,6	24.0	50.1	
	14			
40	2,4	7.2	55.3	40
	2,6	39.3	50.1	
	15			
45	2,4	0	25.4	45
	2,6	0	71.1	
	16			
	2,4	19.2	25.4	
	2,6		71.1	
50	17			50
	2,4	0	21	
	2,6	0	0	
55	18			55
	2,4	0	21	
	2,6	6.1	0	

60 Foams were prepared as follows. The number in parentheses following the ingredient is the parts by weight of said ingredient. 60  
 Formulation A was prepared by admixing NIAX Polyol 1646 (100), distilled water (3), fluorocarbon 11 (3) and silicone L-520 (2) to form mixture 1. NIAX catalyst A-1 (0.2), 65 stannous octoate (0.35), toluene diisocyanate 80/20 (49.5) and either Hylene W (6) or 65

DDI-1410 (6) were admixed to form mixture 2. Mixtures 1 and 2 were combined and stirred for about 10 seconds followed by formation of a very soft polyurethane foam (Foam A).

Formulation B was prepared by admixing NIAX polyol 60-58 (100), distilled water (4), Silicone L-520 (2), and DABCO (0.15) to form mixture 1. N-ethylmorpholine (0.60), stannous octoate (0.15), TDI 80/20 (50) and either Hylene W (6) or DDI-1410 (6) were admixed to form mixture 2. Mixtures 1 and 2 were combined and stirred for about 10 seconds followed by production of a flexible polyurethane foam (Foam B).

Formulation C was prepared by admixing NIAX LG-56 (100), Fryol FR-2 (20), distilled water (4) and Silicone L-520 (1) to form mixture 1. NIAX Catalyst A-1 (0.1), stannous octoate (0.35), TDI 80/20 (50.7) and either Hylene W (6) or DDI-1410 (6) were admixed to form mixture 2. Mixtures 1 and 2 were combined and stirred for about 10 seconds followed by production of a polyurethane foam having flame retardant properties (Foam C).

Formulation D was prepared by admixing Formrez 50 (100), distilled water (3.8), Silicone L-5320 (1.0) and Armeen DM-16-D (0.3) to form mixture 1. N-ethyl morpholine (1.9), TDI 80/20 (44.9) and either Hylene W (5.8) or DDI-1410 (5.8) were admixed to form mixture 2. Mixtures 1 and 2 were combined and stirred for about 10 seconds followed by production of a polyester foam (Foam D).

Formulation E was prepared by admixing XDI-1421 (100), distilled water (3.0) and Silicone L-5320 (0.1) to form mixture 1. Triethylamine (0.15), stannous octoate (0.075) and TDI 80/20 (34.0) were admixed with either Hylene W (5.36) or DDI-1410 (5.36) to form mixture 2. Mixtures 1 and 2 were combined with stirring for about 10 seconds to produce a hydrophilic polyurethane foam (Foam E).

Analysis of the foams of Table II to obtain the residual aromatic amine values was carried out using thin layer chromatography in a method very similar to that described by Kottman (J. A. O. A. C., 49 (5), 954-959 (1966)). Visualization using ultraviolet light was aided by spraying the plates with "Fluram" (Registered Trade Mark; 4-phenylspiro[furan-2(3H),1'-phthalan]-3,3'-dione), by Roche Diagnostics).

In the analytical method a foam sample weighing 1-2 g (weighed to the nearest mg) is covered with 75 ml of methanol in a 250 ml beaker and soaked for 5 minutes with occasional compression. The methanol is decanted by squeezing the foam as completely as possible. This procedure is repeated twice with fresh methanol, and the combined extracts are concentrated to 25 ml for further analysis.

Standard solutions of 2,4- and 2,6-toluene diamine (hereinafter TDA) are prepared in methanol and contain 20, 16, 12, 8, 4 and 2 µg/ml. The standard solutions and the unknown extract (using 20 microlitres of each) are spotted at 7 positions equidistant from each other with each spot being 3 cm from the bottom of a standard 20 cm × 20 cm silica gel TLC plate. The unknown occupies the seventh position at one side of the plate. After the spots have dried, the plate is placed in a developing tank containing 120 ml of chloroform, 33 ml of ethyl acetate, 20 ml of ethanol and 7 ml of glacial acetic acid. Development takes about one hour and is complete when the developing solution reaches a line 15 cm above the bottom of the plate.

The plate is dried in a horizontal position for 5-10 minutes and then sprayed uniformly in a vertical position with a 0.015% solution of Fluram in acetone. The spots which appear approximately 6 cm (2,4-isomer) and 8 cm (2,6-isomer) above the bottom of the plate can be located with ultraviolet light, e.g. a long-wave hand-held BLAK RAY model UVL-60 from Ultraviolet Products, Inc. The sides of the plate are marked to indicate the line through which the plate is to be scanned.

The plate is placed in an Aminco-Bowman Spectrophoto Fluorimeter (Model J4-8427) with a Model J10-280 photomultiplier microphotometer having a strip chart recorder with a 10 millivolt full-scale output attached thereto. The excitation wavelength in the scanner is adjusted to 390 nm and the resulting visible light spot is adjusted to scan across the line of TDA spots. The emission wavelength is set at 500 nm. The plate is scanned starting with the strongest standard spot to generate a chart showing relative fluorescence of the TDA isomer spots as a series of curves wherein the light is proportional to the concentration of TDA in the unknown.

Peak heights are measured from the baseline and are plotted. The concentration of TDA in the extract is then calculated from the known concentrations of the standard solutions. This value, expressed as ppm in the original foam, is obtained using the following equation:

$$\text{TDA, ppm in foam} = \frac{(\text{TDA in extract, } \mu\text{g/ml}) (\text{ml extract})}{\text{foam weight, g.}}$$

To illustrate use of the above equation, if a 2.0 g foam sample generates 25.0 ml of concentrated extract containing 5.7 µg/ml of 2,4-TDA, the foam sample contains approximately 71 ppm of 2,4-TDA.

The precision of the above method is ± 30% at a level of 20 ppm.

*Examples 19-25**Use of Bis(3-methyl-4-isocyanatocyclohexyl)methane as Scavenger for Aromatic Amines*

- 5 Various amounts of bis(3-methyl-4-isocyanatocyclohexyl)methane were admixed with two different hydrophilic urethane prepolymers (Prepolymers F and G) prior to foaming. Foaming was carried out by admixing the prepolymer (100 parts), water (100 parts) and a surfactant (2 parts). The surfactant employed was Pluronic L-62 (BASF/Wyandotte). The resulting foams were analysed for their residual content of aromatic amines according to the method set forth in Examples 9-18, and the results are set forth in Table III.
- 10 Prepolymer F was prepared by admixing polyethylene glycol (M.W. = 1,000) with TMOP. Sufficient TDI was added to cap 95% of the hydroxyl groups present followed by further addition of TDI to provide a theoretical excess of 10% TDI. Following the initial addition of TDI, the admixture was allowed to react for several hours before the final 15% TDI was added. The mole ratio of PEG 1,000/TMOP was 2/1.
- 15 Prepolymer G was prepared following the same general procedure as Prepolymer F with the exception that the PEG 1,000/TMOP ratio was 2/0.66. Also, only 92% TDI was added during the first addition. Following a reaction period, an additional 13% TDI was added. In control 1 and Examples 19-22, Prepolymer F was employed. In control 2 and Examples 23-25, Prepolymer G was employed.
- 20

TABLE III

Example	Parts Diisocyanate Per 100 Parts by weight Prepolymer	Residual Aromatic Amine (PPM)		
		Wet <sup>2</sup>	Air Dry <sup>3</sup> Overnight	30 Minute <sup>4</sup> Forced Air Drying
Control 1	0	15.6	27.2	7.5
19	1.0	0	0	0
20	0.5	0	0	0
21	0.25	8.9	14.2	0
22	1 part <sup>1</sup>	0	13.1	0
Control 2	0	26.0	23.4	10.6
23	1.0	0	0	0
24	0.5	0	0	0
25	0.25	0	0	0

50 <sup>1</sup>Foam prepared by machine equipped with a mixing head. 50

<sup>2</sup>Foam was analyzed when wet immediately after foaming.

<sup>3</sup>Foam was analyzed after drying in air overnight.

<sup>4</sup>Foam was analyzed after drying for 30 minutes with forced air at 60-70°C.

## WHAT WE CLAIM IS:

- 55 1. A process for preparing a fluid-permeable (as hereinbefore defined) polyurethane foam derived from an aromatic poly-isocyanate which comprises incorporating a scavenger for aromatic amine either in:
- 60 (a) a mixture of an aromatic poly-isocyanate, a polyether or polyester polyol and water in which case the index of said scavenger in the mixture is from 0.01 to 4 and the index of said aromatic poly-isocyanate in the mixture is from 110 to 96, or
- 65 (b) a mixture of a prepolymer comprising polyether or polyester units capped by an aromatic poly-isocyanate, and water, in which case the scavenger is present in an amount not more than 8 parts by weight based on the weight of the functional groups of the scavenger per 100 parts by weight of said prepolymer, and causing the resulting mixture to react, or in (c) the foam obtained by reacting a mixture as defined under (a) or (b), which

mixture need not contain scavenger.

2. A process according to claim 1 in which the scavenger exhibits a reaction rate with water which is less than  $10^{-2}$  times the reaction rate of the aromatic poly-isocyanate with water.
- 5 3. A process according to claim 2 in which the scavenger is an aliphatic isocyanate. 5
4. A process according to claim 3 in which the aliphatic isocyanate is 4,4'-methylenebiscyclohexyl diisocyanate, isophorone diisocyanate, bis (3-methyl-4-isocyanatocyclohexyl)methane, tris (6-isocyanatohexamethylene)- biuret or an isocyanate derivative of a condensed fatty acid.
- 10 5. A process according to any one of the preceding claims in which the foam is dried 10 after preparation.
6. A process according to any one of the preceding claims for preparing a hydrophilic polyurethane foam.
- 15 7. A process according to any one of the preceding claims in which the scavenger is 15 incorporated into a mixture as defined under (b).
8. A process according to claim 7 in which the scavenger exhibits a reaction rate with water which is less than  $10^{-3}$  times the reaction rate of the aromatic polyisocyanate with water.
- 20 9. A process according to claim 7 or 8 in which the urethane prepolymer is the reaction 20 product of a polyoxyalkylene polyol wherein at least 40 mole % of the oxyalkylene units are oxyethylene and an aromatic polyisocyanate.
10. A process according to claim 9 in which at least 60 mole % of the oxyalkylene units are oxyethylene.
- 25 11. A process according to any of claims 7 to 10 in which the urethane prepolymer is 25 the reaction product of a polyoxyethylene polyol with a monomeric alcohol having at least 3 hydroxyl groups per molecule, capped with an aromatic poly-isocyanate.
12. A process according to claim 11 in which the alcohol is an aliphatic alcohol having 3 hydroxyl groups per molecule and the polyol is a polyoxvethylene glycol.
- 30 13. A process according to any one of claims 3 to 12 in which the aliphatic isocyanate is 30 present in an amount from 0.1 to 4% by weight of said prepolymer.
14. A process according to any one of claims 7 to 13 in which the water is present in an amount from 0.4 to 1000/mole  $H_2O$ /mole of NCO groups.
15. A process according to any one of claims 7 to 14 in which the water is present in an amount from 6.5 to 390 mole  $H_2O$ /mole of NCO groups.
- 35 16. A process according to any one of claims 1 to 6 in which the scavenger is 35 incorporated into a mixture as defined under (a).
17. A process according to claim 16 in which the polyol is a polyether.
18. A process according to claim 17 in which the polyol is a hydrophilic polyether.
- 40 19. A process according to claim 18 in which the polyol is a polyoxyalkylene polyol in 40 which at least 40 mole % of the oxyalkylene units are oxvethylene.
20. A process according to claim 19 in which at least 60 mole % of the oxyalkylene units are oxyethylene.
21. A process according to any one of claims 18 to 20 in which the polyether is a reaction product of a polyoxyethylene polyol with an aliphatic alcohol having at least 3 45 hydroxyl groups per mole.
22. A process according to claim 15 in which the polyol is a polyester. 45
23. A process according to any one of claims 16 to 21 in which the water is present in an amount from 0.40 to 0.55 mole  $H_2O$ /mole of NCO groups.
- 50 24. A process according to any one of claims 16 to 22 in which the water is present in an 50 amount from 6.5 to 390 mole  $H_2O$ /mole of NCO groups.
25. A process according to any one of claims 16 to 23 in which the index of the aromatic poly-isocyanate in the mixture is from 99.8 to 96.
26. A process according to claim 1 substantially as hereinbefore described.
- 55 27. A process according to claim 1 substantially as described in any one of Examples 1 55 to 4 and 6 to 25.
28. A fluid-permeable polyurethane foam whenever prepared by a process as claimed in any one of the preceding claims.
29. A composition for preparing a polyurethane foam comprising:
  - (a) an aliphatic isocyanate and
  - 60 (b) a hydrophilic urethane prepolymer having polyether backbone segments capped 60 with an aromatic polyisocyanate, the amount of aliphatic isocyanate in said mixture being not more than 8 parts by weight based on the weight of the functional groups of the aliphatic isocyanate per 100 parts by weight of said prepolymer.
- 65 30. A composition according to claim 29 in which the urethane prepolymer is the 65 reaction product of a mixture of a polyoxyethylene polyol with an aliphatic alcohol having

at least 3 hydroxyl groups per molecule, said hydroxyl groups being capped with an aromatic polyisocyanate.

31. A composition according to claim 30 in which the polyoxyethylene polyol is a polyethylene glycol and the aliphatic alcohol has 3 hydroxyl groups per molecule.

5 32. A composition according to any one of claims 29 to 31 in which the aliphatic isocyanate is 4,4'-methylene-biscyclohexyl diisocyanate, isophorone diisocyanate, bis(3-methyl-4-isocyanatocyclohexyl)methane, tris (6-isocyanatohexamethylene)-biuret or an isocyanate derivative of a condensed fatty acid. 5

10 33. A composition according to any one of claims 29 to 32 in which the aliphatic isocyanate is present in an amount from 0.1 to 4% by weight of said prepolymer. 10

34. A composition according to claim 29 substantially as hereinbefore described.

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